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The pure rotational spectrum of TiS ($X^3\Delta_r$) at submillimeter wavelengths

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ABSTRACT

The pure rotational spectrum of TiS in its $X^3\Delta_r$ ground state has been measured using millimeter–wave direct-absorption techniques in the frequency range of 313–425 GHz. This free radical was created by the reaction of titanium vapor, produced in a high-temperature Broida-type oven, with H_2S. Eight to ten rotational transitions were recorded for the main titanium isotopologue, ^{48}TiS, in the $v = 0$ and $v = 1$ levels, as well as for the $v = 0$ state of ^{46}TiS, observed in natural abundance (^{48}Ti:^{46}Ti = 74:8). All three Ω components were observed in almost every recorded transition, with no evidence for lambda-doubling. The data were fit with a Hund's case(a) Hamiltonian, and rotational, spin–orbit, and spin–spin constants were determined, as well as equilibrium parameters for ^{48}TiS. Relatively few fine structure parameters were needed for the analysis of TiS (A, A_D, and λ), unlike other 3d metal species. The rotational pattern of the three fine structure components suggests the presence of a nearby excited $^1\Delta$ state, lying ~3000 cm^{-1} higher in energy. From the equilibrium parameters, the dissociation energy for TiS was estimated to be ~5.1 eV, in reasonable agreement with past thermochemical data.

1. Introduction

Titanium sulfide plays a significant role in a variety of scientific areas. The disulfide form, TiS_2, is an excellent high-temperature lubricant, primarily because of its layered structure, where titanium cations occupy octahedral sites between layers of sulfide anions [1]. The lubricating properties arise from the weak van der Waals interaction between the layers. TiS_2 is also a semiconductor material, and is widely used as the active cathode component in lithium batteries [2]. Titanium sulfide complexes have been shown to activate H_2 [3], and TiS clusters have been created with interesting geometries, stabilized by bridging oxygen atoms [4]. TiS has also been observed in the gas-phase in the atmospheres of S-type stars via its A–X and E–X electronic transitions near 1 μm [5], suggesting it may be detectable in circumstellar ejecta. Clearly, it is important to understand TiS at the most fundamental (monomer) level [6]. If simple properties of this species are understood, they can be generalized to more complex, bulk systems.

For several decades, various optical transitions of TiS have been measured, starting in 1968, when Clements and Barrow recorded the $C^3\Delta_r$–$X^3\Delta_r$ band of this radical in the infrared [7]. These authors were the first to identify the ground state term of TiS as $X^3\Delta_r$, obtaining spectra for all three spin components and performing a rotational analysis. The molecule was then further characterized using Fourier-transform infrared methods by Jonsson and Launila, who measured the $A^3\Phi$–$X^3\Delta$, $E^3\Pi$–$X^3\Delta$, and $C^3\Delta$–$X^3\Delta$ bands in the regions 6000–8600 and 10000–12600 cm^{-1} [8]. Laser induced fluorescence studies of TiS were subsequently conducted by the Cheung group, who employed a supersonic jet/laser ablation source; Ran et al. measured the lower J transitions of the $C^3\Delta$–$X^3\Delta$ band in the 743–863 nm region [9], while Cheung et al. found twenty-one sub-bands which were assigned to the $b^1\Pi$–$X^3\Delta$, $B^3\Pi_0$–$X^3\Delta_1$, and $C^3\Delta$–$X^3\Delta$ transitions [10]. From their data, Cheung et al. determined that the $v = 0$, 1, and 2 levels of the $C^3\Delta_1$ sub-band were highly perturbed by the close-lying $b^1\Pi$ state.

Here we present the first measurement of the pure rotational spectrum of TiS in the $X^3\Delta_r$ ground state. Rotational transitions in all three spin components of the $v = 0$ and $v = 1$ vibrational levels were recorded for ^{48}TiS using millimeter-wave direct-absorption techniques, as well as lines arising from the $v = 0$ state of ^{46}TiS. From these data, the spectroscopic constants have been refined, including equilibrium parameters. Here we present our data, its analysis, and interpretation of the constants in terms of the nearby excited electronic states.

2. Experimental

The spectrum of TiS was measured utilizing one of the quasi-optical millimeter/sub-millimeter spectrometers of the Ziurys

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group. The details of the instrument are described elsewhere [11]. The instrument consists of a radiation source, a free-space gas cell, and a detector. The radiation sources are phase-locked Gunn-oscillator/varacter multiplier combinations, which cover the frequency range 65–850 GHz. Using a polarizing grid and two offset ellipsoidal mirrors, the radiation is quasi-optically directed into the double-pass, steel reaction cell and then to the detector, a helium-cooled, InSb hot-electron bolometer. A pathlength modulator, placed at the beam waist between the two mirrors, is employed to improve baseline stability.

The TiS radical was created from the reaction of titanium vapor and H_2S. To produce the metal vapor, small titanium rods about 1″ long (ESPI: 99.9%) were melted in a Broida-type oven, modified to withstand higher temperatures (m.p. (Ti) = 1668 °C). Modifications included the use of boron nitride crucibles in place of the usual alumina ones, as well as employing molybdenum rods for the oven electrodes, instead of ones constructed of stainless steel. The oven also had to be packed with alumina pieces and the crucible wrapped with zirconia felt, in order to contain the heat. Such adaptations were previously used in the study of TiF [12]. About 1–3 mTorr of H_2S, added over the top of the oven, produced the best TiS signals. Five mTorr of argon carrier gas was also added underneath the oven, which helped to control the melting rate of the titanium.

Final measurements of the rotational transitions were made from an average of one scan in increasing frequency, and the other in decreasing frequency, covering the same 5 MHz range. Gaussian curves were then fit to the line profiles to obtain the center frequency. Typical line widths were ~0.7–1.6 MHz over the frequency range of 313–425 GHz. The instrumental accuracy is estimated to be ±50 kHz.

3. Results and analysis

The initial search for TiS was conducted by continuously scanning the entire range 380–420 GHz, based on frequency estimates using the constants of Cheung et al. [10]. In these data, a pattern of four repeating lines was readily found. Three of these features were attributed to the spin components of a $^3\Delta$ pattern, while the fourth line was identified as arising from the $\Omega = 1$ component of the $v = 1$ level of TiS. Based on this pattern, the $\Omega = 2$ and $\Omega = 3$ components of the $v = 1$ state of TiS were quickly identified. Some remaining weaker features had a similar triplet structure, and were found to be due to ^{46}TiS, in the natural abundance of titanium (^{48}Ti:^{46}Ti = 74:8). Sufficient signal-to-noise could not be achieved to locate the ^{47}TiS or ^{49}TiS isotopologues, which would have provided valuable hyperfine information. There was no discernable lambda-doubling splitting in any of the spectral data.

Once the spectrum of TiS was identified, additional transitions were located and measured. For ^{48}TiS, 10 rotational $J + 1 \leftarrow J$ transitions were recorded in the $v = 0$ state and nine for the $v = 1$ excited level, while eight transitions were measured for the ^{46}Ti isotopologue ($v = 0$), as listed in Table 1. All three spin components were observed for the majority of transitions. In total, 77 lines were measured over the range 310–425 GHz.

Fig. 1 displays a stick diagram of the $J = 34 \leftarrow 33$ transition near 414 GHz for the $v = 0$ and $v = 1$ states of ^{48}TiS and the $v = 0$ state of ^{46}TiS. The relative intensities are also indicated, which were clearly useful in identifying the Ω quantum numbers. As shown in the figure, the splitting between the three spin components was found to be fairly regular. The $\Omega = 1$ and $\Omega = 2$ components are separated by ~1.8 GHz for the $J = 34 \leftarrow 33$ transition, while the separation between the $\Omega = 2$ and $\Omega = 3$ components is ~1.6 GHz. For the $J = 29 \leftarrow 28$ transition, the splittings are ~1.5 and ~1.3 GHz.

Representative spectra for ^{48}TiS are shown in Fig. 2, which displays the three spin components of the $J = 30 \leftarrow 29$ transition near 363 GHz. There are two frequency breaks in the figure in order to show all three lines. Each component appears as a single feature, with no evidence of lambda-doubling splittings. The relative intensities between the three spin components indicate a rotational temperature near 500 K.

The data sets for the $v = 0$ and $v = 1$ states of ^{48}TiS and ^{46}TiS were individually analyzed with the following Hund's case(a) effective Hamiltonian:

$$\hat{H}_{\mathrm{eff}} = \hat{H}_{\mathrm{rot}} + \hat{H}_{\mathrm{so}} + \hat{H}_{\mathrm{ss}} \tag{1}$$

The terms describe molecular frame rotation, spin–orbit coupling, and spin–spin interactions. The spectra were fit with an non-linear least-squares routine, HUNDA, developed by Brown. For each data set, rotational (B and D), spin–orbit (A and A_D), and spin–spin (λ) constants were determined, and these results are shown in Table 2. The rms values for the ^{48}TiS fits are 12 and 16 kHz for the $v = 0$ and $v = 1$ states, respectively, and 28 kHz for ^{46}TiS. Surprisingly, λ_D and higher order centrifugal distortion terms to the fine structure constants were not required to achieve these rms values, unlike other 3d species such as NiCN or TiCl$^+$ [13,14]. The rotational constants derived here are in excellent agreement with those determined from optical measurements [8,10], although previous fits held many of the spin parameter to fixed values. Our fitted A value of 47.4 cm^{-1} agrees well with that determined by Cheung et al. from effective B constants (48.9 cm^{-1}) [10]. The spin–spin parameter found in this work (~1.11 cm^{-1}), on the other hand, is about a factor of two less than that derived by Jonsson and Launila (2.68 cm^{-1}), who based their analysis on the A–X, C–X, and E–X electronic transitions [8]. However, a direct comparison between the two analyses is not feasible because the spin–orbit parameter, A, was fixed at 50 cm^{-1} in the Jonsson and Launila fit [8], and they included the additional parameters λ_D, γ, and γ_D, but not A_D.

Based on the $v = 1$ and $v = 0$ data for ^{48}TiS, equilibrium parameters B_e, D_e, α_e, and β_e were calculated using a least-squares analysis, from which an equilibrium bond length was also derived. These parameters are also listed in Table 2. The harmonic vibrational frequency, ω_e, and anharmonic correction, $\omega_e x_e$, were additionally estimated using the Kratzer and Pekeris approximations, see [15–17]. Finally, the dissociation energy was calculated from the harmonic and anharmonic potential terms. The equilibrium parameters and vibrational constants are in excellent agreement with those of Jonsson and Launila [8], as shown in the table.

4. Discussion

The pure rotational spectra obtained in this work clearly support the TiS ground state assignment as X$^3\Delta_r$ ground state. The spectral analysis required very few modeling parameters, with excellent rms values, as well, for both isotopologues. The simplicity of the analysis may partly result from lack of nearby excited electronic states. The closest known excited ones are the $E^3\Pi$ and $A^3\Phi$ states at energies of 7730 and 7980 cm^{-1}, respectively [8], followed by the $b^1\Pi$, $B^3\Pi$, and $C^3\Delta$ states near ~12,000 cm^{-1}. However, a more likely scenario is that the individual interactions of these states with the ground state cancel each other.

The spacing between the three spin components of the rotational spectra obtained for TiS in this work is not completely symmetrical, however (see Fig. 1). As found in the X$^3\Delta$ state of FeC [18], the $\Omega = 2$ line of TiS appears to be shifted to higher frequency relative to the other two components. This effect may be the result of the nearby isoconfigurational $a^1\Delta$ state. Although this state has not been studied experimentally, calculations by Kaledin, McCord, and